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Applied Catalysis A: General 132 (1995) 127–140

APPLIED CATALYSIS
A: GENERAL

Alkali metal salts and ammonium salts of Keggin-type heteropolyacids as solid acid catalysts for liquid-phase Friedel–Crafts reactions

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Received 19 April 1995; revised 23 June 1995; accepted 27 June 1995

Abstract

The possibility of using a heteropolyacid salt as solid acid catalyst for liquid-phase Friedel–Crafts reactions was investigated through extensive examinations on various kinds of the salt prepared from different combinations of Keggin anions and their counter cations including ammonium ion. The catalytic behavior of the salt was discussed in relation to acidity, surface area, porosity, and thermal stability. Of the different kinds of insoluble acidic salt, K, Rb, Cs, and ammonium salts were mesoporous materials with large surface area (50–170 $m^2\ g^{-1}$), strong acidity ($H_0 < -8.2$), and large pore volume (0.3–0.5 ml g^{-1}). Particularly, $K_{2.5}H_{0.5}PW_{12}O_{40}$, $Rb_{2.5}H_{0.5}PW_{12}O_{40}$, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$, $K_2H_2SiW_{12}O_{40}$, $Cs_2H_2SiW_{12}O_{40}$, and $(NH_4)_2HPW_{12}O_{40}$ worked as efficient solid acid catalysts for liquid-phase Friedel–Crafts alkylation of benzene with benzyl chloride, and some of them could also be effectively applied to the acylation of *p*-xylene with benzoyl chloride or benzoic anhydride. The salt catalysts were much more active than HY, LaY, Nafion-H and Zn-promoted montmorillonite.

Keywords: Heteropolyacid; Solid acid catalyst; Friedel–Crafts reaction; Benzylation; Benzoylation

1. Introduction

Aluminum chloride, boron trifluoride, and sulfuric acid are widely used as efficient homogeneous acid catalysts for the liquid-phase Friedel–Crafts alkylation and acylation using alkyl halides, acyl halides, carboxylic acids and their anhydrides. These homogeneous acids, however, pose several problems of high toxicity, cor-

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SSDI 0926-860X(95)00167-0

rosion, spent acid disposal, necessity of using more than stoichiometric amounts, and difficult separation and reuse. Many solid acids including Nafion-H, zeolite [1], clay montmorillonite [2–5], silica–alumina, sulfate-doped metal oxides [6], and heteropolyacids and their salts [7–9] have been investigated as alternatives for the conventional problematic homogeneous acids catalysts, but none of them is suitably applicable to acylation reactions in polar organic media without deactivation. Concerning heteropoly compounds, Misono and Okuhara showed a high catalytic activity of insoluble acidic Cs salt of 12-tungstophosphoric acid for the alkylation of aromatic hydrocarbon with alkene in nonpolar reaction media [7,8]. We previously reported efficient catalysis of silica-supported heteropolyacid for the liquid-phase alkylation of benzene with alkene and alkyl halide, but the supported catalyst was not appropriate for the acylation using acyl halide because of the dissolution of heteropolyacid [9]. We have also demonstrated that acidic Cs salt of 12-tungstophosphoric acid works efficiently as an insoluble solid acid catalyst for the alkylation of benzene and the acylation of *p*-xylene using benzyl chloride and benzoyl chloride, respectively, owing to its strong acidity and highly porous character [10]. The objective of this work was to investigate the possibility of heteropolyacid salt as solid acid catalyst for liquid-phase Friedel–Crafts reactions through extensive examination on various kinds of salt prepared in different combinations of the Keggin anions and their counter cations including ammonium ion. The catalytic behavior of the salt was discussed in relation to acidity, surface area, porosity, and thermal stability.

2. Experimental

2.1. Catalyst preparation

Alkali metal salt and ammonium salt of heteropolyacid were prepared by adding dropwise a required amount of the corresponding aqueous alkali metal carbonate or ammonium carbonate (0.47 M) to aqueous heteropolyacid (0.75 M) at room temperature. Lithium and sodium salts were all water soluble with all the sorts of heteropoly anions employed, but the other metal salts were obtained as precipitates, except for some potassium salts of 12-tungstosilicic acid. The reaction mixture was aged for 20 h at room temperature, followed by evaporation, drying in vacuum (25 Torr) at 45°C, and finally calcination at 300°C for 3 h under a reduced pressure (25 Torr).

2.2. Friedel–Crafts reactions

The alkylation of benzene with benzyl chloride and the acylation of *p*-xylene with benzoyl chloride were chosen as the test reactions to estimate catalytic activity. The reactions were carried out in a Pyrex flask (30 ml) containing the salt catalyst

(60 mesh pass) and the reactants with vigorous stirring under a stream of nitrogen to remove HCl liberated during the course of the reaction. It was confirmed that the average size of the catalyst particles (60 mesh pass) was small enough to exclude rate limitations by mass transfer, since the same reaction results were obtained over smaller catalyst particles (200 mesh pass). After the reaction, the catalyst was removed by filtration through a Celite pad, followed by washing with diethyl ether to desorb the products remaining in the catalyst. The recovered products were diphenylmethane and 2,5-dimethylbenzo-phenone for the benzylation and the benzoylation, respectively, and were determined by gas chromatography using a Silicone SE-30 column (2 m) and n-tridecane as an internal standard.

2.3. *Catalyst characterization*

Elemental analysis of heteropolyacid salt was performed by means of X-ray fluorescence analysis (XRF) for K, Rb, Cs and W, atomic absorption spectrometry (AAS) for Li, Na, K, Rb and Cs, and the induced couple plasma (ICP) method for Mo and W. The nitrogen adsorption at 78 K over the salt samples was measured, and surface area and pore size distribution were calculated from their adsorption isotherms. The change in the Keggin structure of heteropolyacid salt during calcination and reaction was checked by means of IR spectrometry. The thermal properties of the heteropolyacid salt were measured by thermogravimetric and differential thermal analyses (TG and DTA).

3. Results and discussion

3.1. *Alkali metal salt of 12-tungstophosphoric acid*

According to qualitative estimation by Hammett indicators, all the acidic alkali metal salts of 12-tungstophosphoric acid were strong solid acids having an acid strength of less than -8.2 in terms of H_0 function. Fig. 1 illustrates the change in catalytic activity of the alkali metal salt ($M_xH_{3-x}PW_{12}O_{40}$) for the benzylation of benzene and the benzoylation of *p*-xylene with the cation content denoted by x. The catalytic activity of the Na salt decreased monotonously with increasing Na content for both the benzylation and the benzoylation because of the decrease in acidity. For K, Rb, and Cs salts, however, the activity first decreased with increasing x between 0 and 2, then jumped to attain a maximum at $x=2.5$, except for the benzoylation activity observed with the K salt. Such a characteristic pattern of activity change with the cation content was first reported by Misono et al. concerning the dehydration of 2-propanol and the conversion of dimethyl ether in the vapor phase over Cs salt of 12-tungstophosphoric acid [11–13]. Although the acidic alkali metal salts, as well as the parent free acid $H_3PW_{12}O_{40}$, are protonic acids in nature, they worked as efficient acid catalysts to activate benzyl chloride and

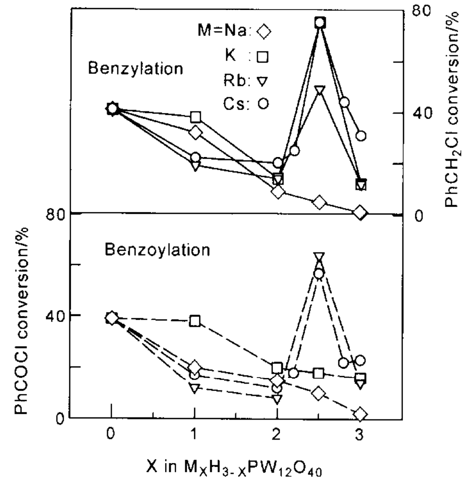

Fig. 1. Catalytic activity of 12-tungstophosphates for benzylation of benzene and benzoylation of *p*-xylene. Benzene/$PhCH_2Cl$/catalyst = 100/5/0.02 mmol, reflux 2 h; *p*-xylene/PhCOCl/catalyst = 100/5/0.01 mmol, reflux 2 h.

benzoyl chloride whose effective promoters are usually Lewis acids. In contrast, typical strong protonic acids such as sulfuric and perchloric acids were quite inactive for the present benzylation and benzoylation. The reason is that heteropoly anion, $PW_{12}O_{40}^{3-}$ has the ability to stabilize cationic intermediates [14], in this case, benzyl and benzoyl cations, whereas simple oxoanions such as sulfate and perchlorate anions are incapable of stabilizing such carbocations. The turnover numbers of the salt catalysts for the benzylation and the benzoylation ranged from 100 to 320 mol^{-1}.

The change in surface area for alkali metal salt of $H_3PW_{12}O_{40}$ with the cation content x is shown in Fig. 2. As for Li and Na salts, their surface areas were as small as less than 10 m^2 g^{-1} with all values of x. It should be noted that on the whole surface area of alkali metal salt of $H_3PW_{12}O_{40}$ increases with the ionic radii of the metal cation.

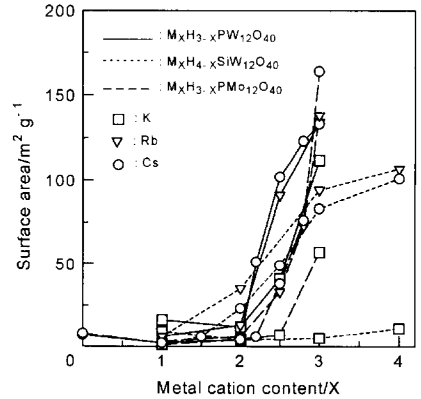

Fig. 2. Effect of metal cation content of heteropolyacid salt on surface area.

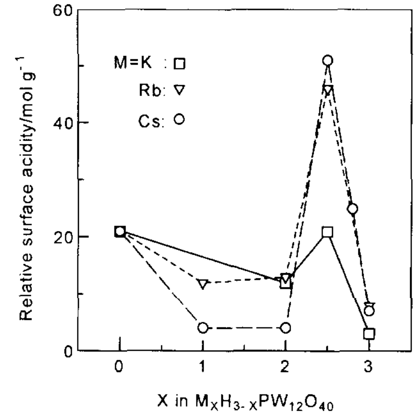

Fig. 3. Relative surface acidity of 12-tungstophosphates.

Sharp increase in surface area observed with K, Rb, and Cs salts beyond $x = 2.0$ corresponds with the increase in catalytic activity depicted in Fig. 1. Such peculiar pattern of the activity change with the cation content x could be interpreted by the change in the surface acidity of catalyst which means the amount of the acid sites on the catalyst surface, as Misono and Okuhara pointed out concerning the vapor-phase conversion of dimethyl ether [11–13] and the liquid-phase decomposition of cyclohexyl acetate [15] over Cs salt of $H_3PW_{12}O_{40}$. Indeed, as shown in Fig. 3, the change in the relative surface acidity reproduced well the change in catalytic activity with the cation content, where the relative surface acidity was calculated as the product of the specific surface area and the bulk acidity of the salt, assuming that the composition of the salt was uniform throughout the surface and the bulk. The uniformity of the bulk composition for $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ has recently been shown by Okuhara et al. through NMR measurement [16]. In the present study, the bulk acidity (moles of proton per unit weight of salt) was calculated from the salt composition. The composition determined by XRF analysis of the Cs/W atomic ratio, which agreed with the composition calculated from the quantities of reagents charged at the salt preparation (Table 1), was adopted for Cs salt. Concerning K and Rb salts, the compositions calculated from the amounts of reagents were taken.

No dissolution of catalytically active species from the salt was observed in the course of the benzylation and the benzoylation, since both reactions ceased completely if the salt was removed from the reactor during the reaction. It was confirmed by IR measurement that the Keggin structure of the salt was completely retained during the reaction showing no changes in the absorption bands characteristic of the Keggin structure (P–O: 1080 cm^{-1}, W=O: 985 cm^{-1}, W–O–W_{corner}: 887 cm^{-1}, W–O–W_{edge}: 807 cm^{-1}).

The pore size distribution of the most active salts ($M_{2.5}H_{0.5}PW_{12}O_{40}$, M = K, Rb, and Cs) is illustrated in Fig. 4. Particularly, $Rb_{2.5}H_{0.5}PW_{12}O_{40}$ and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ are highly porous materials with mesopores of 2–7 nm diameter in average. The surface areas of the salts were consistent with their mesopore structures, since their nitrogen adsorption isotherms were very close to the BET

Table 1
Cation content of heteropolyacid salt

$Cs_xH_{3-x}PW_{12}O_{40}$		$Cs_xH_{4-x}SiW_{12}O_{40}$		$Cs_xH_{3-x}PMo_{12}O_{40}$		$(NH_4)_xH_{3-x}PW_{12}O_{40}$	
x[a]	Cs content[b]	x[a]	Cs content[b]	x[a]	Cs content[b]	x[a]	NH_4 content[c]
1.0	1.00	1.0	1.00	1.0	1.00	1.0	1.09
2.0	1.88	1.5	–	2.0	1.86	2.0	1.91
2.5	2.52	2.0	1.99	2.2	–	2.5	2.56
3.0	2.95	2.5	–	2.5	2.53	3.0	2.58
> 3.0[d]	3.64	3.0	2.99	3.0	2.63	> 3.0[d]	3.01
		4.0	4.06				

[a] Calculated from the composition of reagents charged at the salt preparation.
[b] Determined by XRF analysis.
[c] Determined by thermogravimetric analysis.
[d] Prepared by adding an excess amount of aqueous Cs_2CO_3 or ammonia.

type. The mesopore structure is probably formed by the arrangement of fine primary particles of salt crystallites. Indeed, the SEM picture of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (Fig. 5) tells that the salt consists of fine particles of 10 nm diameter in average. $K_{2.5}H_{0.5}PW_{12}O_{40}$ was much less active for the benzoylation than $Rb_{2.5}H_{0.5}PW_{12}O_{40}$ and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (Fig. 1), which suggests that the highly porous latter two salts favored the benzoylation since the benzoylation appeared to take place not only on the surface but also in the bulk near the surface owing to highly polar nature of benzoyl chloride molecules. The other salts with a cation content of less than 2 in terms of x in $M_xH_{3-x}PW_{12}O_{40}$, as well as the parent acid ($x = 0$), showed smaller

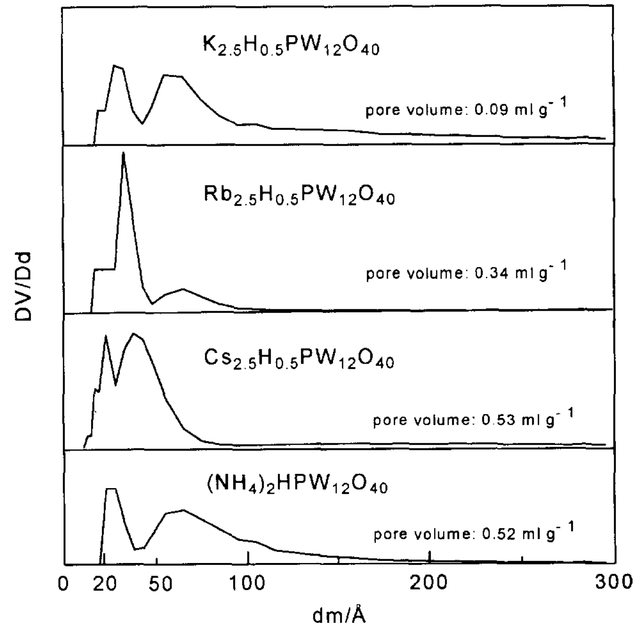

Fig. 4. Pore-size distribution of 12-tungstophosphates.

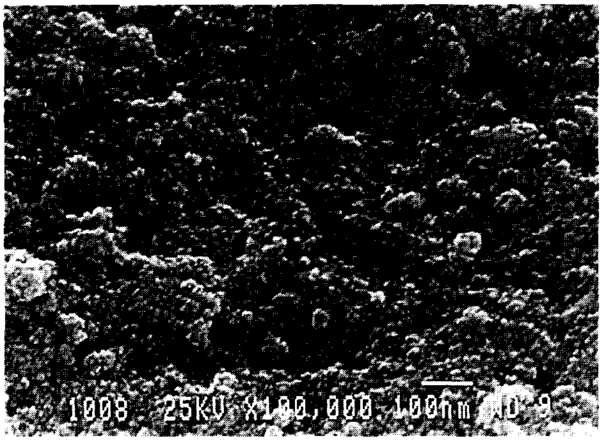

Fig. 5. SEM picture of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$.

surface area and smaller pore volume owing to the large size of the crystallites (20–200 nm). The efficient catalytic performance observed with $Rb_{2.5}H_{0.5}PW_{12}O_{40}$ and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is, therefore, closely associated with their mesoporous structures being built of fine primary particles to afford large pore volume and large surface area.

The DTA profile of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was shown in Fig. 6, comparing with the parent acid $H_3PW_{12}O_{40}$. In addition to a broad endothermic peak until around 200°C due to dehydration of crystalline water, a small exothermic change and a sharp endothermic peak were observed at around 600°C and 1013°C, respectively. The latter peak denotes melting of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ [17]. $Cs_xH_{3-x}PW_{12}O_{40}$ with an x

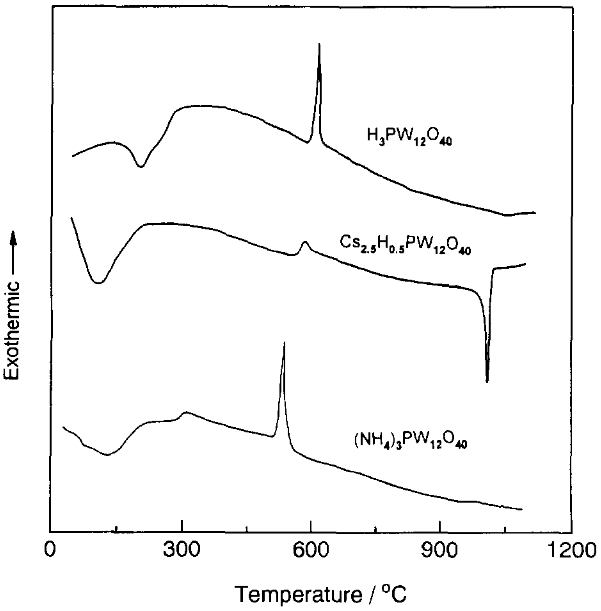

Fig. 6. DTA profiles of 12-tungstophosphoric acid and its cesium and ammonium salts.

Table 2
Friedel–Crafts reactions over $H_3PW_{12}O_{40}$ and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$

Reaction	Product yield/%	
	$H_3PW_{12}O_{40}$	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$
Benzene + benzyl chloride[a]	22	60
Benzene + benzyl alcohol[b]	48	34
p-Xylene + benzoyl chloride[c]	39	57
p-Xylene + benzoic anhydride[d]	3	57
Mesitylene + octanoyl chloride[c]	44	80

[a] Benzene/$PhCH_2Cl$/catalyst = 100/5/0.02 mmol, reflux (80°C) 2 h.
[b] Benzene/$PhCH_2OH$/catalyst = 100/5/0.02 mmol, reflux (80°C) 2 h.
[c] *p*-Xylene/PhCOCl/catalyst = 100/5/0.01 mmol, reflux (138°C) 2 h.
[d] *p*-Xylene/$(PhCO)_2O$/catalyst = 100/5/0.01 mmol, reflux (138°C) 2 h.
[e] Mesitylene/$CH_3(CH_2)_6COCl$/catalyst = 100/5/0.01 mmol, reflux (183°C) 2 h.

value of more than 1.5 including neutral salt ($x = 3$) showed almost the same melting point, and the Keggin structure was retained still after melting, whereas $H_3PW_{12}O_{40}$ and $CsH_2PW_{12}O_{40}$ decomposed at around 600°C showing a sharp exothermic DTA peak. The small exothermic peak of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ at 600°C may be due to partial decomposition of the acid sites, since the catalytic activity drastically reduced when the salt was calcined at high temperatures beyond 500°C. $K_{2.5}H_{0.5}PW_{12}O_{40}$ and $Rb_{2.5}H_{0.5}PW_{12}O_{40}$ showed almost the same thermal durability as $Cs_{2.5}H_{0.5}PW_{12}O_{40}$; their melting points were 898 and 976°C, respectively.

Table 2 lists the catalytic activity of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ for several liquid-phase Friedel–Crafts reactions, as compared with the parent free acid $H_3PW_{12}O_{40}$. The salt catalyst was much more active than the free acid for the benzylation with benzyl chloride and the acylation of aromatic hydrocarbons with benzoic anhydride and octanoyl chloride. In the benzylation, the salt catalysts could be repeatedly used without deactivation. In the benzoylation, however, deactivation was observed, which was caused by strong adsorption of benzoic acid as a by-product produced during the reaction.

3.2. Alkali metal salts of 12-tungstosilicic and 12-molybdophosphoric acids

Li and Na salts of 12-tungstosilicic and 12-molybdophosphoric acids were all water soluble. K salt of 12-tungstosilicic acid ($K_xH_{4-x}SiW_{12}O_{40}$) became water soluble when x was less than 2. These water-soluble salts were catalytically inactive because of their small surface area of less than 10 m^2 g^{-1}. As for the Cs salts of 12-tungstosilicic and 12-molybdophosphoric acids, the compositions determined through XRF analysis agreed with those calculated from the quantities of reagents charged at the salt preparation (Table 1). All insoluble acidic salts were strong solid acids having acid strength of less than -8.2 in terms of H_0 function.

The catalytic activity of K, Rb, and Cs salts of 12-tungstosilicic and 12-molybdophosphoric acids is shown in Fig. 7 and Fig. 8, respectively, for both the ben-

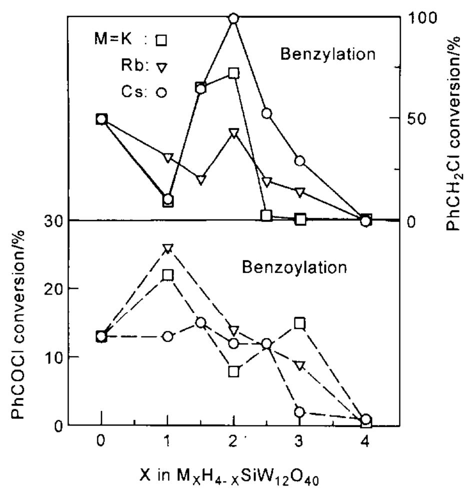

Fig. 7. Catalytic activity of 12-tungstosilicates for benzylation of benzene and benzoylation of p-xylene. Benzene/$PhCH_2Cl$/catalyst = 100/5/0.02 mmol, reflux 2 h; p-xylene/PhCOCl/catalyst = 100/5/0.01 mmol, reflux 2 h.

zylation and the benzoylation. In Fig. 2, the change in surface area with the cation content is depicted. Regarding the benzylation, the maximum activity was obtained at a cation content of $x=2$ for K and Cs salts of 12-tungstosilicic acid, and $x=2.8$ for Cs salt of 12-molybdophosphoric acid. Unlike the salt of 12-tungstophosphoric acid, there was no correlation between the catalytic activity and the surface acidity for the salts of 12-tungstosilicic and 12-molybdophosphoric acids, possibly because their chemical compositions were not uniform throughout the surface and the bulk. Catalytically active $Cs_3HSiW_{12}O_{40}$ salt was a porous material with pore sizes between 2–5 nm and a pore volume of 0.33 ml g^{-1}. The salts of 12-tungstosilicic and 12-molybdophosphoric acids were less active for the benzoylation than the corresponding salt of 12-tungstophosphoric acid. The salt of 12-molybdophosphoric acid, as well as the parent free acid, decomposed and completely dissolved in the reaction medium in the course of the benzoylation reaction, in contrast to the

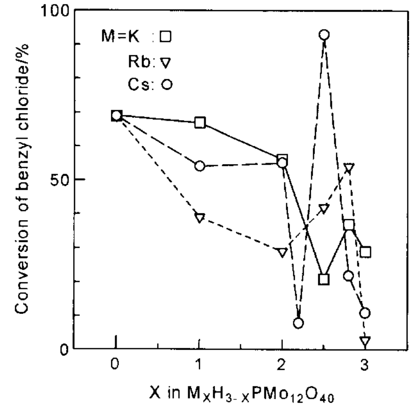

Fig. 8. Catalytic activity of 12-molybdophosphates for benzylation of benzene. Benzene/$PhCH_2Cl$/catalyst = 100/5/0.02 mmol, reflux 2 h.

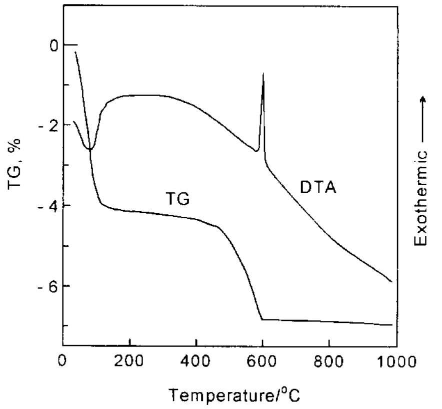

Fig. 9. TG-DTA profile of $(NH_4)_3PW_{12}O_{40}$.

salts of 12-tungstophosphoric and 12-tungstosilicic acids which remained insoluble holding the Keggin structure.

3.3. Ammonium salts of 12-tungstophosphoric and 12-tungstosilicic acids

The catalysis of neutral ammonium and alkylammonium salts of heteropolyacid have been extensively studied on methanol conversion to hydrocarbons [18], disproportionation of alkylbenzene [19], and the conversion of dimethyl ether to alkenes [20] in the vapor phase. There is, however, little information about the application of acidic ammonium salt of heteropolyacid to liquid-phase acid-catalyzed reactions.

Acidic ammonium salt was obtained either directly by adjusting the amount of ammonium carbonate to be reacted with the heteropolyacid, or indirectly by managing the degree of decomposition of neutral ammonium salts prepared beforehand. Fig. 9 illustrates the TG-DTA profile of neutral ammonium 12-tungstophosphate ($(NH_4)_3PW_{12}O_{40}$); the other ammonium salts also showed similar TG-DTA profiles. The reduction in weight on heating followed two stages. The first weight loss, which occurred below 200°C, was due to dehydration of crystalline water, and the second, observed above 300°C, was caused by the decomposition of ammonium ions to liberate ammonia. The decomposition of the Keggin structure took place at 600°C as indicated by the DTA curve. As exemplified in Table 1, the content of ammonium ion in $(NH_4)_xH_{3-x}PW_{12}O_{40}$ determined from the weight loss above 300°C agreed with that calculated from the composition of reagents charged at the salt preparation, except for the neutral salt ($x=3$). The neutral salts, $(NH_4)_3PW_{12}O_{40}$ and $(NH_4)_4SiW_{12}O_{40}$, were obtained only when an excess amount of ammonium carbonate was reacted with heteropolyacid.

The changes in catalytic activity and surface area with the content of ammonium ion are shown in Fig. 10 for the ammonium salts of 12-tungstophosphoric and 12-tungstosilicic acids prepared directly. The acidic ammonium salt was an insoluble and porous material having a relatively large surface area and strong acidity

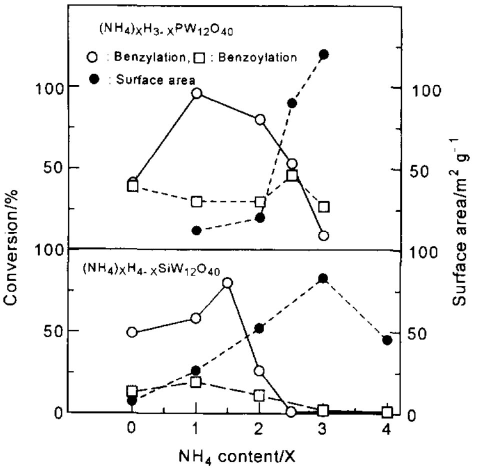

Fig. 10. Catalytic activity and surface area of ammonium 12-tungstophosphate and 12-tungstosilicate for benzylation of benzene and benzoylation of *p*-xylene. Benzene/$PhCH_2Cl$/catalyst = 100/5/0.02 mmol, reflux 2 h; *p*-xylene/PhCOCl/catalyst = 100/5/0.01 mmol, reflux 2 h.

($H_0 < -8.2$). It was more active than the corresponding Cs and Rb salts for the benzylation, but less active for the benzoylation. There was no correlation between the catalytic activity and the surface acidity for both the benzylation and the benzoylation, probably because the composition of ammonium salt was not uniform throughout the surface and the bulk. Fig. 11 depicts the change in the content of ammonium ion in the course of calcination of neutral ammonium salt $(NH_4)_3PW_{12}O_{40}$ performed to form acidic ammonium salt. When treated at 400°C for more than 3 h, $(NH_4)_3PW_{12}O_{40}$ was converted to $(NH_4)_{2.5}H_{0.5}PW_{12}O_{40}$. At 500°C, $(NH_4)_3PW_{12}O_{40}$ decomposed so rapidly that it became difficult to control the content of ammonium ion. In order to obtain active acidic ammonium salt having a higher acidity and larger surface area, calcination at 450°C was preferable and easy to manage. The change in catalytic activity for acidic ammonium salt with the time of calcination at 450°C was shown in Fig. 12. The most active acidic

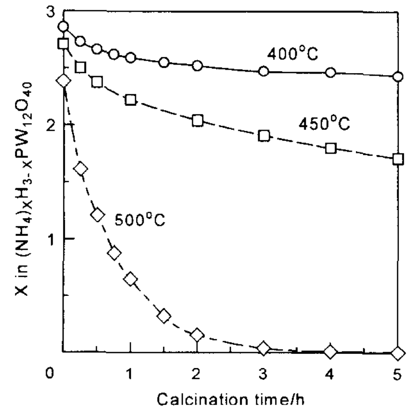

Fig. 11. Change in NH_4 content of ammonium 12-tungstophosphate during calcination. NH_4 content was estimated by thermogravimetric analysis.

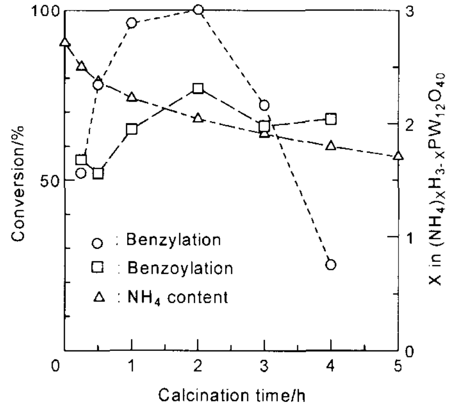

Fig. 12. Changes in catalytic activity and NH_4 content of ammonium 12-tungstophosphate during calcination at 450°C. Benzene/$PhCH_2Cl$/catalyst = 100/5/0.02 mmol, reflux 2 h; *p*-xylene/PhCOCl/catalyst = 100/5/0.01 mmol, reflux 2 h.

ammonium salt $(NH_4)_2HPW_{12}O_{40}$ was obtained after 2 h calcination of $(NH_4)_3PW_{12}O_{40}$. It was a porous material (Fig. 4) with a surface area of 63 m^2 g^{-1} and a pore volume of 0.52 ml g^{-1}, and catalytically more active than the corresponding salt obtained directly (Fig. 10). The control of pore structure by calcination of ammonium or pyridinium salt of the heteropolyacid has also been reported on the conversion of methanol into hydrocarbons [18] and the oxidation of methacrolein [21], respectively. $(NH_4)_2HPW_{12}O_{40}$ did not deteriorate in the benzylation, but gradually reduced its activity in the benzoylation using benzoyl chloride owing to partial dissolution. The benzoylation of *p*-xylene with benzoic anhydride was efficiently catalyzed over $(NH_4)_2HPW_{12}O_{40}$ with no deactivation to give a conversion of 53% under the same reaction condition as described in Table 2.

4. Conclusion

Of the different kinds of insoluble acidic salt of the Keggin-type heteropolyacid, K, Rb, Cs, and ammonium salts were mesoporous materials with large surface area, strong acidity, and large pore volume. Particularly, $K_{2.5}H_{0.5}PW_{12}O_{40}$, $Rb_{2.5}H_{0.5}PW_{12}O_{40}$, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$, $K_2H_2SiW_{12}O_{40}$, $Cs_2H_2SiW_{12}O_{40}$, and $(NH_4)_2HPW_{12}O_{40}$ worked as efficient solid acid catalysts for the liquid-phase Friedel–Crafts alkylation of benzene with benzyl chloride, and some of them could also be effectively applied to the acylation of *p*-xylene with benzoyl chloride or benzoic anhydride. The efficiency of some active salt catalysts for the benzylation and the benzoylation is summarized in Table 3, compared with several representative solid acids reported to be effective for liquid-phase Friedel–Crafts alkylation reactions. The salt catalysts were much more active than HY, LaY and Nafion-H in terms of the activity per unit weight. The clay catalyst, Zn-

Table 3
Activity comparison with other solid acids

Solid acid	Benzylation of benzene[a] PhCH$_2$Cl conversion/%	Benzoylation of *p*-xylene[b] PhCOCl conversion/%
$H_3PW_{12}O_{40}$	41	39
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	75	57
$Cs_{2.5}H_{0.5}PMo_{12}O_{40}$	93	–
$Cs_2H_2SiW_{12}O_{40}$	99	12
$(NH_4)_2HPW_{12}O_{40}^c$	100	77
HY	36	9
LaY	50	9
Nafion-H	24	48
Zn-montmorillonite[d]	100	35[e]

[a] Benzene/benzyl chloride = 100/5 mmol, catalyst 65 mg, reflux, 2 h.
[b] *p*-Xylene/benzoyl chloride = 100/5 mmol, catalyst 35 mg, reflux, 2 h.
[c] Calcined at 450°C, catalyst 30 mg.
[d] Zn^{2+}-ion exchanged montmorillonite.
[e] Catalyst 140 mg.

promoted montmorillonite, showed high activity for the benzylation, but was less effective for the benzoylation than the salt catalysts because considerable deactivation occurred due to dissolution of the active metal components. Similar deactivation was observed also with LaY. The insoluble acidic heteropolyacid salts examined in this study appear to be applicable to several types of liquid-phase acid-catalyzed reactions in relatively polar organic media as efficient and environmentally friendly solid acid catalysts.

Acknowledgements

The present work was supported by a grant-in-aid for Scientific Research No. 06403018 from the Ministry of Education, Science and Culture, Japan. The authors also thank Tokuyama Research Center of Tokuyama Co. Ltd. for the courtesy of SEM measurement of the salt samples.

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